

2-hydroxy,4-methoxy-propiofenone–urea–formaldehyde copolymers and their application as ion-exchangers

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Abstract. Copolymers (2-H, 4-MPPUF) were synthesized by the condensation of 2-hydroxy, 4-methoxy-propiofenone (2-H, 4-MPP), urea (U) and formaldehyde (F) in the presence of HCl and H₂SO₄ as catalyst with varying molar ratios of reacting monomers. The copolymers were characterized by elemental analyses, IR spectra, viscosity and TGA study. Their \bar{M}_n was determined by nonaqueous conductometric titrations and vapour pressure osmometry. Chelation ion-exchange properties have also been studied employing the batch-equilibration method.

Keywords. Chelation ion-exchange; batch equilibration; distribution ratio; copolymers.

1. Introduction

Copolycondensation products of salicylaldehyde with *o*-hydroxybenzyl alcohol or 2,4-dimethylol-4-methylphenol were prepared and studied for their chelation ion-exchange properties (Guivetchi 1963). The resacetophenoneoxime-formaldehyde copolymers have been reported to show chelation ion-exchange properties (Parmar *et al* 1982). Cation exchange copolymer can also be synthesized using resacetophenoneoxime, resorcinol and formaldehyde in alkaline medium (Sykora and Dubosky 1967). Chelating ion-exchange copolymers prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like *o*-amino-phenols, β -resorcylic acid or resorcinol with formaldehyde have been reported earlier (Pennington and Williams 1959; Aristov and Konstantinov 1961; DeGeiso *et al* 1962). Since 2-hydroxy, 4-methoxy propiofenone is a chelating agent, it is obvious that polymers prepared from 2-hydroxy, 4-methoxy propiofenone will be also the subject of extensive investigations for its chelation properties.

We report in this paper the systematic study of the selectivity and capacity of 2-hydroxy, 4-methoxypropiofenone (2-H, 4-MPP)–urea–formaldehyde (F) copolymers (2-H, 4-MPPUF) in ion-exchange reactions.

2. Experimental

2.1 Materials and monomer preparation

All chemicals used were of analytical grade. DMF was used after triple distillation. Pyridine and methanol were purified by conventional chemical methods. 2,4-dihydroxy-

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propiophenone (m.p. 96 °C) was prepared in the laboratory (Brewster and Harris 1930). 2-hydroxy,4-methoxypropiophenone (m.p. 58 °C) was prepared by steam distillation of 2,4-dihydroxypropiophenone with dimethyl sulphate in aqueous sodium carbonate solution (Omer and Hamilton 1937).

2.2 Preparation of 2-H, 4-MPPUF copolymers

A mixture of 2-H, 4-MPPUF 18.09 (0.1 mol), 37% formaldehyde 16.2 ml (0.2 mol) and 2M HCl 50 ml was taken in a round-bottomed flask, equipped with a stirrer, condenser and separating funnel. With good stirring, the contents were refluxed at 60 °C using an oil bath. Subsequently 6.0 g of urea (0.1 mol dissolved in 5 ml H₂O) were added dropwise from the separating funnel and the reaction mixture was then refluxed at 110 °C for 5 h. The solid yellow product obtained was filtered, washed with large amounts of water followed by acetone to remove unreacted 2-H, 4-MPP and urea. It was purified by dissolving in 8% aq. NaOH and reprecipitated by adding 1:1 (v/v) HCl/H₂O with constant stirring. Finally, the copolymer was washed with boiling water and dried. The purified copolymers were finely ground to pass a 200 mesh screen and used in all experiments described in the present paper. Different polymer samples were prepared employing different molar ratios of monomer, urea, formaldehyde and catalysts. The samples and reaction details are given in table 1.

2.3 Measurements

Analyses of C, H and N were carried out on the Coleman C-H and N-analyzer. The number average molecular weights (\bar{M}_n) of copolymers were determined by nonaqueous conductometric titration and vapour pressure osmometry (VPO) using DMF as a solvent and benzil as a calibrant at 71 °C. IR spectra in KBr disks were recorded on a Perkin-Elmer-983 spectrophotometer. The intrinsic viscosities of the copolymers were measured in DMF at 35 °C using an Ubbelohde viscometer. The thermograms TG were recorded on a Du Pont Thermal Analyzer-951. Scans were taken at a heating rate of 10 °C/min. For ion-exchange study the purified copolymer sample 2-H, 4-MPPUF-2 was used. We have adopted the batch equilibration method (Gregor *et al* 1952). The details of the procedure are similar to those reported earlier from this laboratory (Patel and Patel 1988).

3. Results and discussion

3.1 Molecular weight determination

The number average molecular weight \bar{M}_n , determined by nonaqueous conductometric titrations (DeGieso *et al* 1962) and VPO are presented in table 2. The values obtained by both methods are in good agreement. Copolymers synthesised from equimolar proportions of 2-H, 4-MPP and urea have comparatively higher molecular weights in the series. The use of formaldehyde in larger than stoichiometric proportion gave low molecular weight copolymers.

Table 1. Synthesis and analytical data of copolymers.

Copolymers	Reactants			Catalyst 2M		Elemental analysis*			
	2-H,4-MPP (mol)	Urea (mol)	Formaldehyde (mol)	HCl (ml)	H ₂ SO ₄ (ml)	C%	H%	N%	Yield%
2-H,4-MPPUF-1	0.10	0.10	0.10	50.0	—	61.24 (62.55)	6.09 (6.56)	8.36 (8.34)	74
2-H,4-MPPUF-2	0.15	0.10	0.25	63.0	—	59.16 (60.34)	7.90 (7.50)	10.65 (10.90)	82
2-H,4-MPPUF-3	0.10	0.05	0.15	37.5	—	59.95 (58.74)	8.24 (8.36)	9.73 (9.60)	60
2-H,4-MPPUF-4	0.125	0.05	0.175	44.0	—	55.99 (53.36)	5.99 (5.60)	14.19 (14.50)	67
2-H,4-MPPUF-5	0.10	0.10	0.20	—	50.0	57.42 (57.90)	6.03 (6.00)	12.58 (12.70)	70
2-H,4-MPPUF-6	0.15	0.10	0.25	—	63.0	63.43 (62.66)	6.15 (6.34)	5.97 (5.44)	58
2-H,4-MPPUF-7	0.10	0.05	0.15	—	37.5	60.77 (61.40)	6.09 (6.37)	8.92 (8.67)	63
2-H,4-MPPUF-8	0.125	0.05	0.175	—	44.0	58.58 (59.30)	6.05 (6.12)	11.24 (11.56)	48

* Numbers in parentheses are calculated values.

Table 2. Molecular weight determination, viscometric data of copolymers.

Copolymers	Molecular weight (\bar{M}_n)		Intrinsic viscosity ^c [η] $\times 10^2$ (dl/g)	Huggins constant K_1	Kraemers constant K_2	$K_1 + K_2$
	VPO ^a	Conductometric titration				
2-H,4-MPPUF-1	1182	1258	6.15	0.362	0.107	0.469
2-H,4-MPPUF-2	1366	1470	6.56	0.400	0.189	0.589
2-H,4-MPPUF-3	852	925	5.14	0.782	-0.229	0.553
2-H,4-MPPUF-4	933	997	4.90	0.321	0.280	0.601
2-H,4-MPPUF-5	712	700	3.96	0.225	0.265	0.490
2-H,4-MPPUF-6	998	1057	6.48	0.138	0.391	0.529
2-H,4-MPPUF-7	1276	1354	5.54	0.118	0.312	0.430
2-H,4-MPPUF-8	617	695	3.12	0.339	0.172	0.511

^aIn DMF at 71°C; ^bin pyridine against standard sodium methoxide (NaOMe) in pyridine; ^cin DMF at 35 \pm 1°C.

3.2 Viscometric study

The viscometric measurement were carried out in DMF and reduced viscosity *vs* concentration (3.0 to 1.152 g·dl⁻¹) was plotted for each set of data. The intrinsic viscosity [η] was determined from the corresponding linear plots. The following equations were used to determine the Huggin and the Kraemer constants respectively.

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C, \text{ (Huggin 1942),} \quad (1)$$

$$\ln(\eta_r/C) = [\eta] - K_2[\eta]^2 C, \text{ (Kraemer 1938).} \quad (2)$$

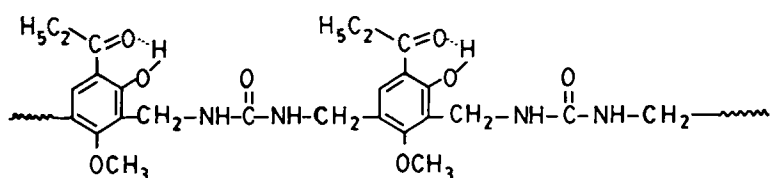
In accordance with the above relations the plots of η_{sp}/C and $\ln \eta_r/C$ against C were linear giving the slopes K_1 and K_2 respectively. Intercepts on the viscosity function axis gave [η] values in both the plots. The calculated values of constants K_1 and K_2 (table 2) in most of the cases satisfy the relation $K_1 + K_2 = 0.5$ (Huggin 1942). It has been observed that the copolymer having higher \bar{M}_n shows higher values of [η].

3.3 IR spectra

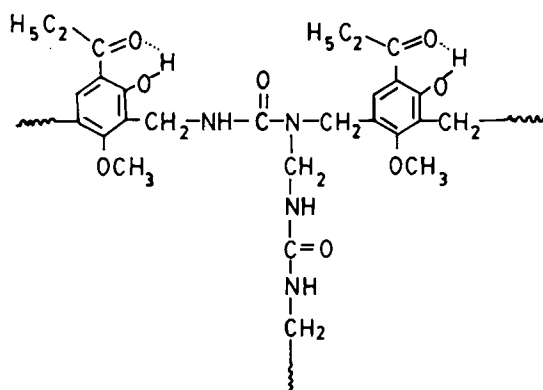
All the copolymers give rise to nearly similar spectra. The reaction of urea and formaldehyde with 2-H,4-MPP in the presence of acid catalyst results in an electrophilic substitution on the aromatic ring. Here, the preferred attack of urea and CH₂O would be at positions 3 and 5 as they are ortho with respect to the

electron-releasing OH group and meta to the electron-withdrawing $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}_2\text{H}_5 \end{array}$ group. The strong C=O stretch at 1650 cm⁻¹ and a weak band around 2740 cm⁻¹ indicate an intramolecular H-bond (Nakanishi 1964). The bands at 2940, 1470 and 735 cm⁻¹ suggest the presence of methylene bridges in the copolymers (Gupta and Malik 1969). The out-of-plane C-H bending band around 900 cm⁻¹ is due to penta-substituted phenyl ring (McMurry and Vernon 1952). The absorption bands at 1450 and 1490 cm⁻¹ are attributed to C=C stretching (aromatic) vibrations (Bellamy 1975).

On the basis of the nature and reactive positions of the monomers, elemental analyses, molecular weights and infrared spectra, and also taking into account the linear structure of other substituted phenol-formaldehyde copolymers (DeGeiso *et al* 1962) and the linear branched nature of urea-formaldehyde copolymer (Slonim and Alekseye 1977), the structures proposed for the copolymers are of two types: Linear structure (I) and branched structure (II) which may sparsely cross-link through the N-atom of the urea unit. Thus, the distribution of n monomer units along the copolymer chain would be random.



(I)



(II)

3.4 TG analysis

The examination of the results of TGA (table 3) reveals that each copolymer sample undergoes degradation in a single step. Copolymers are thermally stable up to 200 °C. All the copolymers undergo thermal degradation at slow rates in the beginning upto 250 °C. Decomposition is completed at 600 °C where 85 to 95% weight loss is observed. Copolymers prepared using equimolar proportions of reactants are thermally more stable. The Broido method was applied to the TG data to determine the energy of activation (Broido 1969).

3.5 Ion-exchanging properties

The results of the batch equilibrium study carried out with copolymer sample 2-H, 4-MPPUF-2 are presented in tables 4, 5 and 6.

Examination of data given in table 4 reveals that the amount of Cu^{2+} , UO_2^{2+} and Fe^{3+} ions taken up by a given amount of copolymer sample increases with increasing

Table 3. TG and IR spectral data.

Copolymer	%weight loss at temperature (°C)					Activation energy E (kcal/mol)	Important IR frequency wavenumber (cm ⁻¹)	Probable assignment
	100	200	300	400	500			
2-H,4-MPPUF-2	2.9	10.1	31.7	40.4	60.7	89.5	1650(<i>b</i>) 2940(<i>w</i>) 1470(<i>m</i>) 740(<i>m</i>)	$\nu_{C=O}$ -CH ₂ - bridge
2-H,4-MPPUF-6	2.5	50.0	65.0	70.0	89.0	95.0	1630(<i>w</i>) 1610(<i>w</i>) 1680(<i>w</i>)	C=C stretch + NH bend
2-H,4-MPPUF-7	1.0	20.3	27.4	50.3	71.0	85.0	3200-3600 (<i>m, b</i>)	-OH in-plane bending
2-H,4-MPPUF-8	3.0	7.0	48.0	79.0	90.0	—	1650-1470(<i>m</i>) 1380(<i>sh</i>)	-C=C stretch -COC ₂ H ₅ bend

Abbreviations; *b* – broad; *w* – weak; *m* – medium; *sh* – shoulder.

Table 4. Evaluation of the effect of different electrolytes in the uptake of metal ions.M(NO₃)₂ = 0.1 mol/l^a.Resin = 25 mg^b.

Metal ion	Electrolyte (mol/l)	pH	Weight in meq × 10 of the metal ion uptake in the presence of			
			NaClO ₄	NaCl	NaNO ₃	Na ₂ SO ₄
Cu ²⁺	1.00	6.0	0.47	0.51	0.50	0.56
	0.50		0.35	0.40	0.41	0.60
	0.10		0.29	0.36	0.32	0.66
	0.05		0.22	0.29	0.29	0.72
	0.01		0.17	0.27	0.17	0.75
Ni ²⁺	1.00	5.0	0.68	0.45	0.36	0.55
	0.50		0.71	0.55	0.40	0.60
	0.10		0.76	0.64	0.44	0.66
	0.05		0.83	0.70	0.52	0.75
	0.01		0.89	0.76	0.58	0.84
Co ²⁺	1.00	5.0	0.44	0.24	0.26	0.36
	0.50		0.50	0.28	0.30	0.42
	0.10		0.56	0.33	0.40	0.49
	0.05		0.63	0.40	0.46	0.56
	0.01		0.71	0.47	0.59	0.66
UO ₂ ²⁺	1.00	4.0	0.70	0.65	0.32	0.17
	0.50		0.62	0.61	0.27	0.30
	0.10		0.56	0.54	0.22	0.38
	0.05		0.51	0.47	0.15	0.45
	0.01		0.45	0.40	0.11	0.56
Fe ³⁺	1.00	2.5	0.60	0.99	0.62	0.43
	0.50		0.51	0.93	0.59	0.50
	0.10		0.46	0.82	0.50	0.55
	0.05		0.39	0.77	0.37	0.62
	0.01		0.36	0.56	0.32	0.66

^a Volume of electrolyte solution: 44 ml;

Volume of metal ion solution: 2 ml;

Time: 24 h; Temp. 30°C.

^b 2-H,4-MPPUF-2.

concentration of ClO₄⁻, NO₃⁻ and Cl⁻ and decreases with increasing concentration of SO₄²⁻, whereas the uptake of Co²⁺ and Ni²⁺ ions by the above copolymer increases with decreasing concentration of ClO₄⁻, NO₃⁻, Cl⁻ and SO₄²⁻. This may be explained in terms of stability constants of complexes which Fe³⁺, UO₂²⁺, Cu²⁺, Ni²⁺ and Co²⁺ form with these ligands (Bjerrum *et al* 1958; Cotton and Wilkinson 1972; Davydov and Plate 1975). Sulphate might form strong chelates while ClO₄⁻, NO₃⁻ and Cl⁻ might form weak chelates with Cu²⁺, UO₂²⁺ and Fe³⁺ ions and therefore might not be expected to influence the position of the Cu²⁺, UO₂²⁺ and Fe³⁺ chelate equilibrium to the extent expected for the sulphate (Patel and Patel 1988), whereas Co²⁺ and Ni²⁺ ions might form strong chelates with ClO₄⁻, Cl⁻ and NO₃⁻ and hence their metal uptake increases with decreasing concentration of electrolyte (Parmar *et al* 1982).

Table 5. Comparison of the rate of metal (M^{n+}) ion uptake^a.

Metal ion	Percentage of metal ion uptake ^b at different times (h)						
	0.5	1.0	2.0	3.0	4.0	5.0	6.0
Cu^{2+}	13.2	26.7	36.4	42.7	60.3	72.4	81.3
Ni^{2+}	46.3	56.4	62.1	70.8	81.3	89.1	96.6
Co^{2+}	38.4	42.3	55.7	62.0	80.3	89.9	99.1
UO_2^{2+}	56.4	62.3	79.4	94.4	100.0	—	—
Fe^{3+}	47.4	74.3	76.4	82.1	91.3	—	—

^a $M(NO_3)_2 = 0.1 \text{ mol l}^{-1}$; Volume: 2 ml; $NaNO_3 = 1 \text{ mol l}^{-1}$; Volume: 44 ml pH = 3.0; Temp. 30 °C.

^b % metal ion uptake =

$$\frac{\text{amount of metal ion adsorbed} \times 100}{\text{amount of metal ion adsorbed at equilibrium}}$$

Table 6. Distribution ratios D of different metal ions as a function of the pH.

Metal ion	Distribution ratio of the metal ions at different pH values							
	1.25	1.50	2.00	2.50	3.00	4.00	5.00	6.00
Cu^{2+}	—	—	—	32	78	112	170	870
Ni^{2+}	—	—	—	22	57	68	181	—
Co^{2+}	—	—	—	58	66	78	107	—
UO_2^{2+}	—	—	—	53	72	96	210	—
Fe^{3+}	—	21	45	72	198	—	—	—

$$^*D = \frac{\text{meq. of metal on the copolymer}}{\text{meq. of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of dry copolymer (g)}}$$

Temp.: 30°C; time: 24 h; copolymer: 25 mg; $M(NO_3)_2$: 0.1 mol/l/2 ml; $NaNO_3$: 1.0 mol/l, 44 ml.

The rate of metal adsorption of 2-H, 4-MPPUF-2 was measured to determine the shortest period of time for which equilibration could be carried out while operating as close to equilibrium conditions as possible. Table 5 shows the dependence of the rate of metal ion uptake on the nature of the metal. Fe^{3+} and UO_2^{2+} ions required slightly more than four hours for the establishment of equilibrium. In experiments with solutions containing UO_2^{2+} and Fe^{3+} ions more than 60% equilibrium was established in the first hour. The rate of metal uptake follows the order



The effect of pH on the amount of metal ion distributed between two phases can be explained by the results shown in table 6. The results indicate that the relative amounts of metal ions taken up by the copolymer increase with increasing pH of the

medium. In case of Fe^{3+} and UO_2^{2+} the highest value of working pH was 3.0 and 5.0 respectively. The lower distribution ratio of Fe^{3+} as compared to that of UO_2^{2+} may be attributed to the steric hindrance imposed by the polymer matrix which inhibits the complexation of the $\text{Fe}^{3+} d^2sp^3$ orbital with 3 mers of 2-H, 4-MPPUF-2 as opposed to the formation of the chelate of Fe^{3+} with monomeric 2-H, 4-MPP. UO_2^{2+} only needs 2 mers of 2-H, 4-MPPUF-2 for complexation of its coordination requirement, which is easily accomplished (DeGeiso *et al* 1962). Co^{2+} and Ni^{2+} have low distribution ratios in the range of pH 4 to 6. This could be attributed to the low stability constants i.e. weak ligand stabilization energies of the metal complexes (Cotton and Wilkinson 1972). The possible order to selectivity of a cation exchange copolymer for a divalent metal ion would be $\text{Pd} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$ (Irving and Williams 1953). In the present study the observed order of distribution ratios of divalent ions measured in the range of 3 to 6 pH was found to be $\text{Cu}^{2+} > \text{UO}_2^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. The results of this study were helpful in selecting the optimum pH for 0 selective uptake of a metal ion from a mixture of different ions. For example, the results suggest the optimum pH value 5.0 for the separation of Co^{2+} and UO_2^{2+} ions, at which the distribution ratio D for Co^{2+} is 107 and that of UO_2^{2+} is 210.

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